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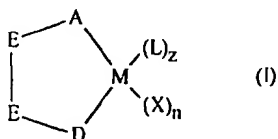
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(54) Catalyst systems for the polymerization and copolymerization of alpha-olefins

(57) Catalyst component for the polymerisation of
alpha-olefins of general formula (I)



Wherein

M is a transition metal of groups 3, 4-10 of the periodic table of the elements. Each X group is equal or different and it is hydride, halogen, alkyl, cycloalkyl, aryl, alkenyl, arylalkyl, arylalkenyl or alkylaryl with 1 to 20 carbon atoms. L is a neutral Lewis base. A is a ring with delocalized π electrons. Each E group is equal to or different from each other and it is BR^{III} , CR^{III}_2 , $\text{SiR}^{\text{III}}_2$, $\text{GeR}^{\text{III}}_2$. D is O, S, PR^{IV} .

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Description

The present invention relates to a new class of organometallic catalysts, to the process for preparation thereof and their use for the polymerisation and copolymerisation of ethylene and alpha-olefins in industrial production plants.

There is a great variety of processes and catalysts useful for the homo- and copolymerization of olefins. Catalytic systems such as Ziegler-Natta are typically able to produce polyolefins with high molecular weight and broad distribution of molecular weight. However, for many industrial applications it is of the greatest importance to obtain polyolefins characterized by high molecular weight and narrow molecular weight distribution. Besides, with these Ziegler-Natta type of catalysts, to obtain copolymers with fit contents of comonomer it is necessary to use high comonomer/monomer molar ratios in the feed and as a consequence the industrial process becomes enormously more expensive.

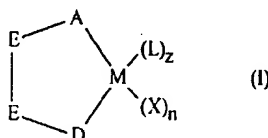
In the last years there has been the development of organometallic catalytic metallocene systems, that, combined with non-coordinative anions, alkylaluminoxanes or boron perfluorinated compounds (US 4542199 and EP 426637) allow to obtain polyolefins with narrow distributions of molecular weight and high molar comonomer contents. However, the molecular weights are not as high as it would be useful to give the polymer the desired properties. Besides, these molecular weights suddenly lower when the comonomer content is increased, or when the polymerization temperature rises.

In EP 416815 and EP 420436 there is the description of a new type of organometallic catalysts in which a transition metal is coordinated to a cyclopentadienyl ring and a heteroatom. These organometallic compounds, when they are activated with alkylaluminoxanes, are able to produce ethylene polymers with high molecular weight and narrow distribution of molecular weight. They moreover own a great effectiveness in comonomer incorporation. However, when the comonomer content of the polymeric chain is increasing, the molecular weight sensibly decreases.

Therefore it is an object of the present invention to provide new compounds useful in the (co)polymerization of alpha-olefins, in particular in the (co)polymerization of ethylene, which can produce polymers with high molecular weight. Besides, these catalysts are especially efficient in the comonomer incorporation, and produce copolymers with totally random distribution of the comonomer.

A further object of the present invention is to provide new useful methods for obtaining catalysts according to the invention. These synthetic methods are novel and more suitable than those already known in the art.

The organo metallic complexes (catalysts) disclosed in the present invention are characterized by the following general formula I:



wherein:

M is a transition metal of groups 3, 4-10 of the periodic table of the elements, lanthanide or actinide, preferably titanium, zirconium or hafnium.

Each X group, equal to or different from each other, is hydrogen, halogen, alkyl, cycloalkyl, aryl, alkenyl, arylalkyl, arylalkenyl or alkylaryl with 1 to 20 carbon atoms, branched or not, the hydrogens of these groups are optionally substituted by SiR_3 , GeR_3 , OR, NR_2 , OSiR_3 groups or any combination thereof wherein R is selected from the group comprising: hydrogen, $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_3\text{-C}_{20}$ cycloalkyl, $\text{C}_6\text{-C}_{20}$ aryl, $\text{C}_7\text{-C}_{20}$ alkenyl, $\text{C}_7\text{-C}_{20}$ arylalkyl, $\text{C}_7\text{-C}_{20}$ arylalkenyl or alkylaryl, branched or linear.

n is a number whose value is: 0, 1, 2 or 3, in order to fill the remaining free valences of the metal M;

L is a neutral Lewis base such as diethylether, tetrahydrofurane, dimethylaniline, aniline, triphenylphosphine, *n*-butylamine, etc.

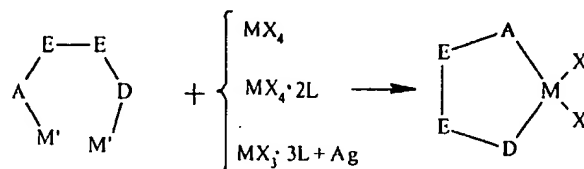
z is a number whose value is: 0, 1, 2 or 3.

A is a ring with delocalized π electrons, that directly coordinates to the transition metal M. A is preferably a cyclopentadienyl type of ring of formula C_5R^1_4 , wherein each R^1 group equal to or different from each other is hydrogen, $\text{C}_1\text{-C}_{20}$ alkyl, $\text{C}_3\text{-C}_{20}$ cycloalkyl, $\text{C}_6\text{-C}_{20}$ aryl, $\text{C}_7\text{-C}_{20}$ alkenyl, $\text{C}_7\text{-C}_{20}$ arylalkyl, $\text{C}_7\text{-C}_{20}$ arylalkenyl or alkylaryl, branched or linear, the hydrogens of these groups is optionally substituted by SiR_3 , GeR_3 , OR, NR_2 , OSiR_3 groups or any combination thereof wherein R is above defined; R^1 is also selected from the group comprising SiR_3 , GeR_3 , OR, NR_2 , OSiR_3 or any combination thereof. Two adjacent R^1 optionally unite in order to form a saturated or unsaturated polycyclic cyclopentadienyl ring such as indenyl, tetrahydroindenyl, fluorenyl or octahydrofluorenyl, optionally substituted by R^1 groups.

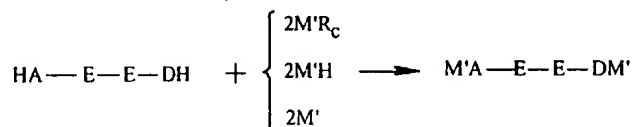
Each E group, equal to or different from each other, is BR^{II} , CR^{III}_2 , SiR^{II}_2 , GeR^{II}_2 . Preferably the bridge E-E is $\text{CR}^{\text{III}}_2\text{-CR}^{\text{III}}_2$ or $\text{CR}^{\text{III}}_2\text{-SiR}^{\text{II}}_2$. Each R^{II} , equal to or different from each other, is hydrogen, alkyl, cycloalkyl, aryl, alkenyl, arylalkyl, arylalkenyl or alkylaryl with 1 to 20 carbon atoms, linear or branched, whose hydrogens are optionally substituted by SiR_3 , GeR_3 , OR, NR_2 , OSiR_3 groups or any combination thereof wherein R is above defined; R^{III} has the same meaning of R^{II} or it is halogen. Besides two groups selected from R^{II} and R^{III} , belonging to different E optionally form a cyclic structure.

D is O, S, PR^{IV} or a neutral ligand which gives two electrons such as: OR^{IV} , SR^{IV} , PR^{IV}_2 . Each R^{IV} , equal to or different from each other, is hydrogen, alkyl, cycloalkyl, aryl, alkenyl, arylalkyl, arylalkenyl or alkylaryl from 1 to 20 carbon atoms, branched or not, whose hydrogens are optionally substituted by SiR_3 , GeR_3 , RO, R_2N , -OSiR_3 groups or any combination thereof wherein R is above defined; moreover it optionally forms a condensed ring through another bond with E. When D is neutral, the bond between M and D is more exactly described as a coordinative-dative bond.

The catalysts component of general formula I, described in the present invention, is suitably prepared through reaction of a compound of general formula $\text{M}'\text{-A-E-E-D-M}'$, wherein M' preferably is Li, Na or K, with a metal M compound, preferably of formula MX_4 or with an adduct of formula $\text{MX}_4\cdot 2\text{L}$, or $\text{MX}_3\cdot 3\text{L}$; where L preferably is a linear or cyclic ether as for example: ethylic ether, tetrahydrofurane, dimethoxyethane, etc, and X is above defined, according to the following scheme.



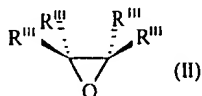
The compound of general formula $\text{M}'\text{-A-E-E-D-M}'$ is suitably prepared through reaction of HA-E-E-DH with two equivalents of an alkyl or aryl alkali metal salt, or with an alkali metal hydride or an alkali metal according the following scheme:



Wherein R_c is $\text{C}_1\text{-C}_{20}$ alkyl or $\text{C}_6\text{-C}_{20}$ aryl.

Alternatively, alkyl magnesium salts, which are obtained in the same way, is used, but using an alkyl magnesium halide instead of alkyl lithium.

When D contains oxygen and the bridging group E-E is $\text{CR}^{\text{III}}_2\text{-CR}^{\text{III}}_2$, the compound HA-E-E-DH can be suitably prepared through the reaction of the alkali metal salt of the cyclic organic compound HA with a compound of general formula II:



Wherein R^{III} has already been defined.

The compounds preferably used are: ethylene oxide, propylene oxide, styrene oxide, cyclopentane oxide, cyclohexane oxide, stilbene oxide.

The method comprises the following steps:

a) contacting the compound (II) with the alkali metal salt of the cyclic organic compound HA, according to the following scheme:



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(2-(cyclopentadienyl) 1-oxo-ethanediyl) titanium dichloride

- (2-(1-indenyl) 1-oxo-ethanediyl) titanium dichloride
 (2-(9-fluorenyl) 1-oxo-ethanediyl) titanium dichloride
 (2-(cyclopentadienyl) 1-oxo-cyclohexanediyl) titanium dichloride
 (2-(cyclopentadienyl) 1-oxo-ethanediyl) zirconium dichloride
 5 (2-(1-indenyl) 1-oxo-ethanediyl) zirconium dichloride
 (2-(9-fluorenyl) 1-oxo-ethanediyl) zirconium dichloride
 (2-(cyclopentadienyl) 1-oxo-cyclohexanediyl) zirconium dichloride
 (2-(cyclopentadienyl) 1-tio-ethanediyl) titanium dichloride
 (2-(1-indenyl) 1-tio-ethanediyl) titanium dichloride
 10 (2-(9-fluorenyl) 1-tio-ethanediyl) titanium dichloride
 (2-(cyclopentadienyl) 1-tio-cyclohexanediyl) titanium dichloride
 (2-(cyclopentadienyl) 1-tio-ethanediyl) zirconium dichloride
 (2-(1-indenyl) 1-tio-ethanediyl) zirconium dichloride
 (2-(9-fluorenyl) 1-tio-ethanediyl) zirconium dichloride
 15 (2-(cyclopentadienyl) 1-tio-cyclohexanediyl) zirconium dichloride

The organometallic catalyst of formula I, can be used in the polymerization and copolymerization of alpha-olefins through the addition of cocatalysts. These cocatalysts are compounds which can form non-coordinative anions, such as alkylaluminoxanes or boron perfluorinated compounds. Representative, but non-limiting, examples are methylaluminoxane, ethylaluminoxane, N,N-dimethylaniliniumtetrakis(pentafluorophenyl)borate, and tris(pentafluorophenyl)borane. In case boron derivatives are used, it is preferable to add to the polymerization medium little quantities of aluminium alkyls (TIBA, TEA, TMA, etc.).

The catalytic systems thus prepared are fit for the polymerization of alpha-olefins with 2 to 20 carbon atoms, in particular for the polymerization of ethylene, and for the copolymerization of ethylene with at least one alpha-olefin with 3 to 20 carbon atoms, such as propylene, 1-butene, 4-methyl-pentene, 1-hexene, etc., with dienes, with cycloalkenes and with styrene. The polymerization can be realized through a process in solution, in suspension, in gas phase or in bulk at high pressure and temperature. When using a suspension process, hydrocarbon solvents, such as branched or linear aliphatic hydrocarbons (hexane, heptane, isobutane, etc.), cyclic hydrocarbons (benzene, toluene, xylene, etc.) or a mixture thereof are used as a reaction medium. The polymerization can be realized between 1 and 4000 atmospheres and temperatures between -60 and 300°C, preferably between 40 and 220°C, and the polymerization time can vary between 20 seconds and 6 hours, according to the process.

The used concentrations of the organometallic catalyst, is from 10^{-7} to 10^{-3} M, preferably from 10^{-6} to 10^{-4} M. The organoaluminum compound (for example an aluminoxane) is used in a concentration from 10^{-4} to 10^{-1} M, preferably from 10^{-3} to 10^{-2} M. However, bigger concentrations of both components are possible as well. When an aluminoxane is used as cocatalyst, the used Al/M molar ratio ranges from 100 to 10000, preferably between 500 and 1500. When a boron compound is used, the molar ratio varies in the range 0.5-10, preferably 0.9-5.

The molecular weight of the obtained polymers can be controlled by varying the concentration of catalyst, cocatalyst and monomer in the polymerization medium, by varying the polymerization temperature as well as by the addition of regulators of the molecular weight such as H_2 . When in the preparation of the catalyst only one type of cocatalyst is used, polymers with narrow distributions of the molecular weight are obtained. However, when several types of catalysts and/or cocatalysts are used, the obtained polymers have broad distribution of molecular weight, including also multimodal distributions.

The copolymerization reaction can be realized by using the same process as the one used in the homopolymerization process, but moreover by feeding the reaction medium with the suitable comonomer or comonomers. The preferred comonomer/monomer molar ratio is comprised between 0.1/1 and 5/1. In this way, copolymers with controlled content and random distribution of comonomer are obtained.

Figure 1 shows some examples of compounds of general formula I wherein D is oxygen or sulphur.

The following examples are described in order to better understand the invention. The materials, the chemical compounds and the conditions used in these examples are illustrative and do not limit the scope of the invention.

50 The average molecular weights in number, weight and distribution were determined through gel permeation chromatography GPC or SEC. The intrinsic viscosities $[\eta]$ were obtained at 145°C through viscosimetric techniques, using as a solvent trichlorobenzene with 0.05% of antioxidant in order to prevent polymer degradation.

EXAMPLE 1

55 a) Preparation of 2-Cyclopentadienyl ethanol

110 g (2.5 mol) of ethylene oxide was added to a solution of 176 g (2 mol) of sodium cyclopentadienide in tetrahy-

drofurane, the reaction was maintained under stirring for 12 hours, then, the resulting suspension was neutralized with an ammonium chloride solution. The organic phase was extracted with hexane and concentrated to dryness, leaving an oil which was distilled, obtaining the compound at a temperature of 40-45°C under reduced pressure of 2.7×10^{-4} bar (0.2 mmHg) (22 g, 0.2 mmoles, yield: 10%). $^1\text{H-NMR}$ (CDCl_3): 6.70-6.00(m,3H), 3.80(m,3H), 2.85(m,2H), 2.60(m, 2H).

b) Preparation of the dilithium salt of 2-cyclopentadienylethanol

33 ml of a solution 2.5 M of butyllithium (82 mmol) in hexane was added to a solution of 4.5 g (41 mmol) of 2-cyclopentadienyl ethanol in ether at -78°C. The formation of a white solid was immediately observed, the reaction was left under stirring for 6 hours. Then, it was concentrated to dryness, obtaining a white oily solid, which was washed with hexane twice, in order to obtain a powdery white solid (4.8 g, 40 mmol, yield: 97%).

c) Preparation of (2-cyclopentadienyl-1-oxo-ethanediyl)titanium dichloride

A suspension of 4.8 g (40 mmol) of the dilithium salt of 2-cyclopentadienylethanol was added to 14.8 g (40 mmol) of titanium trichloride adduct with tetrahydrofuran using tetrahydrofuran as a solvent. It was observed that the suspension darkened and acquired a reddish color. It was maintained under stirring for 2 hours and then 5.7 g (40 mmol) of silver chloride was added. It was left under stirring for 12 hours, then it was brought to dryness and toluene was added, the resulting suspension was filtered and the solution was concentrated to dryness in order to obtain 1.25 g (5.5 mmol) of (2-cyclopentadienyl-1-oxo-ethanediyl) titanium dichloride. $^1\text{H-NMR}$ (CDCl_3): 6.06 (m,2H), 5.77(m,2H), 4.66(t,2H), 2.14 (t,2H). $^{13}\text{C-NMR}$ (CDCl_3): 147.4, 121.1, 118.0, 96.7. MS: $M^+ = 225.9$ (23%).

EXAMPLE 2

To a glass reactor of 1 liter, previously dried and degassed, 600 ml of n-heptane was added. The temperature was raised to 70°C and the solvent was stirred at 1200 rpm. When the thermic equilibrium was achieved, the medium was saturated with ethylene at a pressure of 4 bar. 17 ml of a MAO solution in toluene (1.5 M in total aluminium) was added at 2 bar of ethylene. The pressure was raised to 4 bar and 2 minutes later 0.05 mmol of the organometallic compound described in example 1 was added. The system was fed with ethylene for 15 minutes and then the polymerization was stopped by closing the ethylene flux and adding 20 ml of acidified methanol. 1 g of polyethylene with an intrinsic viscosity of 3.5 dl/g was obtained.

EXAMPLE 3

Ethylene and 1-hexene were copolymerised. For that, the same method as in example 2 was used, but once the solvent had been added and before the reactor was pressurised, 4 ml of dry and just distilled 1-hexene was injected. A MAO solution of 17 ml (1.5 M in total aluminium) in toluene and 0.05 mmol of the catalyst described in example 1, dissolved in toluene, was used. After 15 minutes of polymerization 1.1 g of polyethylene with an intrinsic viscosity of 3.45 dl/g was obtained. The molar content in 1-hexene determined by $^{13}\text{C-NMR}$ was 0.45% distributed at random.

EXAMPLE 4

a) Preparation of 2-indenylethanol

20.1 g (456 mmol) of ethylene oxide was added to 50.2 g (456 mmol) of indenyllithium in ether at -78°C; the immediate formation of a yellowish solid was observed. 2 hours later it was neutralised with a saturated NH_4Cl solution. The organic phase was concentrated to dryness, obtaining a yellowish oil which was distilled at reduced pressure (3.4 bar and 115°C) in order to produce a clear yellow oil. 20.6 g (129 mmol yield: 43%). $^1\text{H-NMR}$ (CDCl_3): 7.50(m,1H), 7.42(m,1H), 7.40(m,1H), 7.33(m,1H), 6.35(m,1H), 4.00(m,2H), 3.47(m,2H), 2.92(m,2H), 2.30(m,1H).

b) Preparation of the 2-indenyl-ethyl tosylate

To a solution of 12.6 g (78.7 mmol) of 2-indenylethanol in dichloromethane, 11 ml (78.7 mmol) of triethylamine and 15 g (78.7 mmol) of tosyl chloride in dichloromethane was added; immediately, a product was observed. The reaction was maintained under stirring for 3 hours and 200 ml of distilled water was added. The organic phase was extracted and it was brought to dryness. The resulting solid was twice washed with hexane in order to give the desired product: 11.6 g (35.2 mmol, yield: 45%). $^1\text{H-NMR}$ (CDCl_3): 7.70(m,2H), 7.20(m,6H), 6.24(m,1H), 4.30(m,2H), 3.25(m,2H), 2.90

(m,2H), 2.36(s,3H).

c) Preparation of 1-*tert*butylamino-2-indenylethane

A solution of 11g (33 mmol) of 2-Indenyl ethyl tosylate was prepared and to that solution 9.65g (132 mmol) of *tert*butylamine was added. The reaction was warmed at 70°C and the formation of a white solid was observed. It was kept under stirring for 24 hours, then it was cooled and the solvent was evaporated and extracted with hexane and the resulting solution concentrated in order to produce a yellowish oil: 4.5 g (21 mmol, yield: 63%). ¹H-NMR (CDCl₃): 7.50 (m,1H), 7.42(m,1H), 7.25(m,2H), 6.30(m,1H), 3.38(m,2H), 2.97(m,2H), 2.83(m,2H), 1.20(s,9H).

d) Preparation of the dilithium salt of 1-*tert*butylamino-2-indenylethane

10.4 ml of a 2.5 M solution of butyllithium (26 mmol) in hexane was added to a solution of 2.8 g (13 mmol) of 1-*tert*butylamino-2-indenylethane in ether at -78°C. The immediate formation of a whitish solid and butane evolution were observed and when room temperature was achieved it was maintained under stirring for 2 hours; then it was concentrated to dryness and the resulting solid was twice washed with hexane in order to give a white powdery solid: 2.9 g (13 mmol, yield: 100%).

e) Preparation of (1-*tert*butylamide-2-indenylethanediy)l) titanium dichloride

A suspension of 2.9 gr (13 mmol) of the dilithium salt of 1-*tert*butylamino-2-indenylethane in toluene were added to a suspension of 2.5 g (13 mmol) of titanium tetrachloride in ether at -78°C. A brown suspension immediately was formed and the reaction was maintained under stirring at room temperature for 12 hours. The resulting suspension was brought to dryness and it was extracted with hexane several times, obtaining an orange-reddish solution that was concentrated for obtaining a red solid: 1.7 g (5 mmol, yield: 38%). ¹H-NMR (CDCl₃): 7.69(m,1H), 7.58(m,1H), 7.32(m,2H), 6.75(m,1H), 6.61(m,1H), 4.60(dm,2H), 3.50(dm,2H), 1.40(s,9H). ¹³C-NMR (CDCl₃): 134.2, 129.0, 128.3, 127.9, 127.1, 126.5, 123.5, 121.4, 109.5, 70.2, 64.4, 28.8, 28.5.

EXAMPLE 5

Preparation of (1-*tert*butylamide 2-indenylethanediy)l)zirconium dichloride

A suspension of 1.7 g (7.7 mmol) of the dilithium salt of 1-*tert*butylamino-2-indenylethane in ether was added to a suspension of 1.8 g (13 mmol) of zirconium tetrachloride in ether at -78°C. A brown-yellowish suspension immediately was formed and it was maintained under stirring at room temperature for 12 hours. The resulting suspension was brought to dryness and it was extracted several times with toluene, obtaining a reddish-orange solution. It was concentrated and a yellow solid was formed: 0.8 g (2 mmoles, yield: 26%). ¹H-NMR (CDCl₃): 7.69(m,1H), 7.58(m,1H), 7.32(m,2H), 6.75(m,1H), 6.61(m,1H), 4.60(dm,2H), 3.50(dm,2H), 1.40(s,9H). ¹³C-NMR (CDCl₃): 134.2, 129.0, 128.3, 127.9, 127.1, 126.5, 123.5, 121.4, 109.5, 70.2, 64.4, 28.8, 28.5.

EXAMPLE 6

a) Preparation of 2-(9-fluorenyl) ethyl tosylate

9 g (205 mmol) of ethylene oxide was added to 33.4 g (200 mmol) of fluorenyl lithium in ether at -78°C; the immediate formation of a yellowish solid was observed. 2 hours later, a solution of 38.2 g (200 mmol) of tosyl chloride in tetrahydrofuran was added and it was observed that the product changed its color up to cream. The reaction was maintained under stirring for 12 hours, later, it was neutralized with an aqueous ammonium chloride solution. The organic phase was extracted and brought to dryness, in order to give an oily solid, which was twice washed with hexane to give the desired compound. (35 g, 96 mmol, yield: 48%). ¹H-NMR (CDCl₃): 7.75(m,4H), 7.40-7.20(m,8H), 4.15-3.90(m,3H), 2.52(s,3H), 2.30(m,2H).

b) Preparation of 1-*tert*butylamino-2-(9-fluorenyl)-ethane

A solution of 10.9 g (30 mmol) of 2-(9-fluorenyl) ethyl tosylate was prepared and to this solution 8.78 g (120 mmol) of *tert*butylamine was added. It was warmed at 70°C and the formation of a white solid was observed. It was maintained under stirring for 24 hours, then it was cooled, the solvent was evaporated, the residue was extracted with hexane and the resulting solution was concentrated to dryness in order to give an orange oil (6.2 g, 23.4 mmol, yield: 78%). ¹H-

NMR (CDCl₃): 7.78(m,2H), 7.54(m,2H), 7.45-7.20(m,4H), 4.07(m,1H), 2.50(m,2H), 2.25(m,2H), 0.95(s,9H).

c) Preparation of dilithium salt of 1-*tert*butylamino-2-(9-fluorenyl)ethane

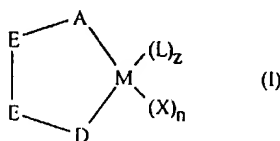
A solution of 8 ml 2.5 M (20 mmol) of butyllithium in hexane was added to a solution of 2.70 g (10 mmol) of 1-*tert*butylamino-2-(9-fluorenyl)-ethane in ether at -78°C. The immediate formation of a whitish solid and butane evolution were observed, it was allowed to warm to room temperature and it was maintained under stirring for 2 hours, it was then concentrated to dryness and the resulting solid was twice washed with hexane in order to give a powdery white solid (2.35 g, 8.5 mmol, yield: 85%).

d) Preparation of [1-*tert*butylamide-2-(9-fluorenyl)-ethanediyl] zirconium dichloride

A suspension of 2.35 g (8.5 mmol) of the dilithium salt of 1-*tert*butylamino-2-(9-fluorenyl)-ethane in toluene was added to a suspension of 2 g (8.6 mmol) of zirconium tetrachloride in toluene at -20°C. A brown-reddish suspension immediately was formed and it was maintained under stirring at room temperature for 12 hours. Then, it was filtered and the resulting yellow solution was concentrated to dryness, producing a yellowish solid (1.1 g, 2.6 mmol, yield: 30%). ¹H-NMR (C₆D₆): 7.83 (m,2H), 7.51(m,2H), 7.15(m,2H), 4.16 (t,2H), 3.20(t,2H), 1.21(s,9H).

Claims

1. Catalyst component for the polymerisation of alpha-olefins of general formula (I)



wherein:

M is a transition metal of groups 3, 4-10 of the periodic table of the elements, lanthanide or actinide; each X group, equal to or different from each other, is hydrogen, halogen, alkyl, cycloalkyl, aryl, alkenyl, arylalkyl, arylalkenyl or alkylaryl with 1 to 20 carbon atoms, branched or not, the hydrogens of these groups are optionally substituted by SiR₃, GeR₃, OR, NR₂, OSiR₃ groups or any combination thereof wherein R is selected from the group comprising: hydrogen, C₁-C₂₀ alkyl, C₃-C₂₀cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkenyl, C₇-C₂₀ arylalkyl, C₇-C₂₀ arylalkenyl or alkylaryl, branched or linear;

n is a number whose value is: 0, 1, 2 or 3, in order to fill the remaining free valences of the metal M; L is a neutral Lewis base;

z is a number whose value is: 0, 1, 2 or 3;

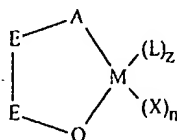
A is a ring with delocalized π electrons, that directly coordinates to the transition metal M; each E group, equal to or different from each other, is BR^{II}, CR^{III}₂, SiR^{II}₂, GeR^{II}₂; each R^{II}, equal to or different from each other, is hydrogen, alkyl, cycloalkyl, aryl, alkenyl, arylalkyl, arylalkenyl or alkylaryl with 1 to 20 carbon atoms, linear or branched, whose hydrogens are optionally substituted by SiR₃, GeR₃, OR, NR₂, OSiR₃ groups or any combination thereof wherein R is above defined; R^{III} has the same meaning of R^{II} or it is halogen; besides two groups selected from R^{II} and R^{III} belonging to different E optionally form a cyclic structure;

D is selected from the group comprising: O, S, PR^{IV} or a neutral ligand selected from the group comprising: OR^{IV}, SR^{IV}, PR^{IV}₂; each R^{IV}, equal to or different from each other, is hydrogen, alkyl, cycloalkyl, aryl, alkenyl, arylalkyl, arylalkenyl or alkylaryl from 1 to 20 carbon atoms, branched or not, whose hydrogens are substituted by SiR₃, GeR₃, OR, NR₂, OSiR₃ groups or any combination thereof wherein R is above defined; or it moreover forms a condensed ring through another bond with E.

2. Catalyst component according to claim 1 wherein A is a cyclopentadienyl type of ring of formula C₅R^I₄, wherein each R^I group, equal to or different from each other, is hydrogen, C₁-C₂₀ alkyl, C₃-C₂₀ cycloalkyl, C₆-C₂₀ aryl, C₇-C₂₀ alkenyl, C₇-C₂₀ arylalkyl, C₇-C₂₀ arylalkenyl or alkylaryl, branched or linear, the hydrogens of these groups are optionally substituted by SiR₃, GeR₃, OR, NR₂, OSiR₃ groups or any combination thereof wherein R is described in claim 1; R^I is also selected from the group comprising SiR₃, GeR₃, OR, NR₂, OSiR₃ groups or any combination

thereof; two adjacent R^I optionally unite in order to form a saturated or unsaturated polycyclic cyclopentadienyl ring, optionally substituted with R^I groups.

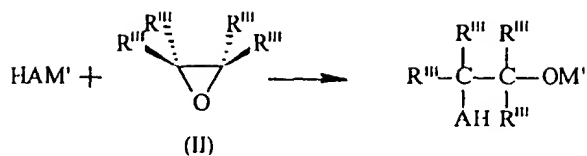
3. Catalyst component according to claim 1-2, wherein M of general formula (I) is selected from the group consisting of zirconium, titanium or hafnium.
4. Catalyst component according to claims 1-3, wherein the bridging group E-E is $CR^{III}_2-CR^{III}_2$.
5. Catalyst system comprising a cocatalyst selected from the group consisting of alkylaluminoxane, modified aluminoxane, boron compounds and a catalyst component according to claims 1-4.
6. Catalyst system according to claim 5 wherein the cocatalyst is selected from the group comprising: methylaluminoxane, ethylaluminoxane, N,N-dimethylaniliniumtetrakis (pentafluorophenyl) borate, and tris(pentafluorophenyl) borane.
7. Process for obtaining polyolefins in solution, in suspension, in gas phase at low and high pressure and temperature or in mass at high pressures and high or low temperatures, characterized by the use of the catalyst according to claims 5-6.
8. Process for obtaining polyolefins according to claim 7, wherein the polymerization temperature varies between -60°C and 300°C , the pressure varies between 1 and 4000 atmospheres, the transition metal concentration varies between 10^{-7} and 10^{-3} M, the cocatalyst is an aluminium organocomplex and the cocatalyst/transition metal molar ratio varies between 10 and 10000.
9. Process for obtaining polyolefins according to claim 7, wherein the polymerization temperature varies between -60°C and 300°C , the pressure varies between 1 and 4000 atmospheres, the transition metal molar concentration varies between 10^{-7} and 10^{-3} , the cocatalyst is a boron compound and the cocatalyst/transition metal molar ratio varies between 0.5 and 10.
10. Process for obtaining polyolefins according to claim 8, characterized in that the polymerization temperature varies between -40°C and 220°C , the pressure varies between 1 and 4000 atmospheres, the transition metal concentration varies between 10^{-6} and 10^{-4} M, the cocatalyst is an aluminium organocomplex and the cocatalyst/transition metal molar ratio varies between 500 and 1500.
11. Process for obtaining polyolefins according to claim 9, characterized in that the polymerization temperature varies between 40°C and 220°C , the pressure varies between 1 and 4000 atmospheres, the transition metal molar concentration varies between 10^{-6} and 10^{-4} , the cocatalyst is a boron compound and the cocatalyst/transition metal molar ratio varies between 0.9 and 5.
12. Process for obtaining polyolefins according to claims 7-11, wherein the monomer is ethylene.
13. Process for obtaining ethylene copolymers according to claims 7-12, wherein the comonomer is selected from the group comprising: propene, 1-butene, 1-hexene, 1-octene, 1-hexadecene, 4-methyl-1-pentene, hexadiene and styrene or mixtures thereof.
14. Process for obtaining the compound of formula:



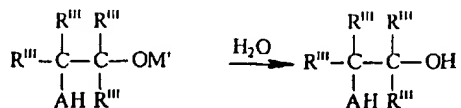
wherein E is CR^{III}_2 and A, M, L, X, z and n are defined in claims 1-4 characterized by the following steps:

- a) contacting the compound (II) with the alkali metal salt of the cyclic organic compound HA, according to the

following scheme:

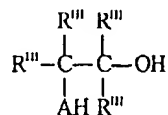


b) treating the reaction product of step a) with water

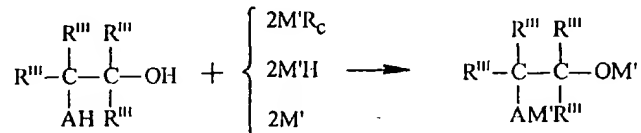


Wherein R^{III} is as above defined and M' is selected from the group comprising Li, Na or K.

c) treating the compound of formula:



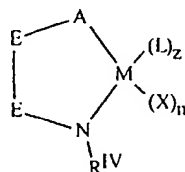
with two equivalents of an alkyl or aryl alkali metal compound, or with an alkali metal hydride or an alkali metal according to the following scheme:



Wherein R_c is C_1 - C_{20} alkyl or C_6 - C_{20} aryl.

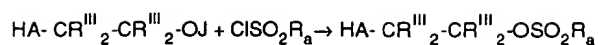
d) contacting the compound of formula $\text{M}'\text{A}-\text{CR}^{\text{III}}_2-\text{CR}^{\text{III}}_2-\text{OM}'$ with a metal M compound, of formula MX_4 or with an adduct of formula $\text{MX}_4 \cdot 2\text{L}$, or $\text{MX}_3 \cdot 3\text{L}$, wherein L is a linear or cyclic ether

15. Process for obtaining a compound of formula:



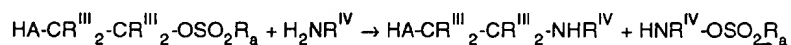
according to claims 12 wherein E is CR^{III}_2 and A, M, L, X, z and n are defined in claims 1-4 characterized by the following steps:

a) reacting a compound of formula $\text{HA}-\text{CR}^{\text{III}}_2-\text{CR}^{\text{III}}_2-\text{OH}$ obtained by step b) of the process of claims 12 or its lithium salt with an alkyl- or aryl-sulphonates according to the scheme:

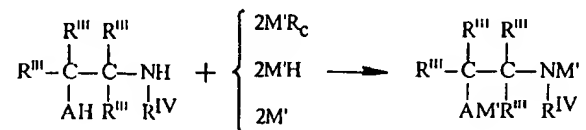


wherein J is lithium or hydrogen R_a is $\text{C}_1\text{-C}_{20}$ alkyl, perfluoralkyl or $\text{C}_6\text{-C}_{20}$ aryl radical;

b) contacting the recovered product of step a) with an excess of an amine of formula $\text{NR}^{\text{IV}}\text{H}_2$ according to the scheme:



c) treating the compound of formula $\text{HA-CR}^{\text{III}}_2\text{-CR}^{\text{III}}_2\text{-NHR}^{\text{IV}}$ with two equivalents of an alkyl or aryl alkali metal salt, or with an alkali metal hydride or an alkali metal according to the following scheme:



Wherein R_c is $\text{C}_1\text{-C}_{20}$ alkyl or $\text{C}_6\text{-C}_{20}$ aryl.

d) contacting the compound of formula $\text{M}'\text{A-CR}^{\text{III}}_2\text{-CR}^{\text{III}}_2\text{-NR}^{\text{IV}}\text{M}'$ with a metal M compound, of formula MX_4 or with an adduct of formula $\text{MX}_4\cdot 2\text{L}$, or $\text{MX}_3\cdot 3\text{L}$, wherein L is a linear or cyclic ether.

Figure 1

